



Valorization of castor seed shell waste as lead adsorbent by treatment with hot phosphoric acid: Optimization and evaluation of adsorption properties[☆]

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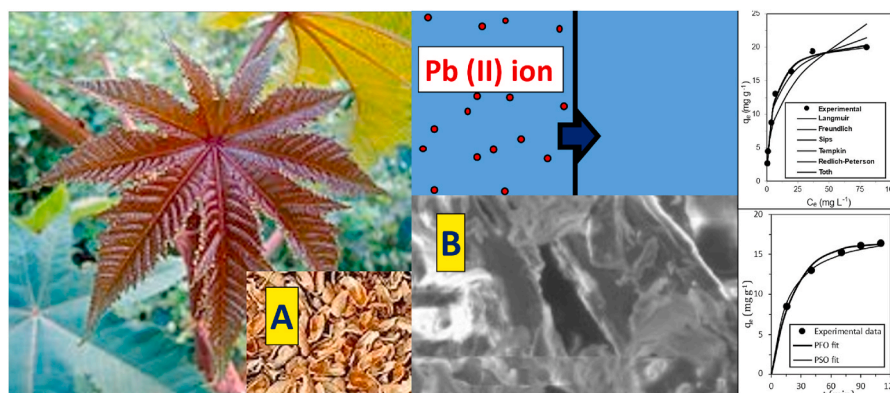
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HIGHLIGHTS

- Hot phosphoric acid was used for treatment castor seed shell wastes.
- The acid-treated biomass was exploited for lead ion removal from waters.
- Kinetic and equilibrium studies demonstrated high potential of the adsorbent for this goal.
- Thermodynamic consideration revealed spontaneity and feasibility of the process.

GRAPHICAL ABSTRACT



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ABSTRACT

Lead is used in many industries such as refining, mining, battery manufacturing, smelting. Releases of lead from these industries is one of the major public health concerns due to widespread persistence in the environment and its resulting poisoning character. In this work, the castor seed shell (CSS) waste was exploited for preparing a

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beneficial bio-adsorbent for removal of Pb(II) ions from water. The raw CSS was modified with H_3PO_4 at different acid concentrations, impregnation ratios, activation times, and temperatures. An optimum adsorption capacity was observed for CSS modified with 2 M acid, 5 mL g^{-1} solid to liquid ratio, treated at 95 °C for 160 min. Exploiting acid modification, the SEM, XRD, and FTIR analyses show some alterations in functional groups and the surface morphology of the biomass. The impacts of physiochemical variables (initial lead ions concentration, pH, adsorbent dose and adsorption time) on the lead removal percentage were investigated, using response surface methodology (RSM). Maximum removal of 72.26% for raw CSS and 97.62% for modified CSS were obtained at an initial lead concentration (50 mg L^{-1}), pH (5.7), adsorption time (123 min) and adsorbent dosage (1.1 g/100 mL). Isothermal and kinetics models were fitted to adsorption equilibrium data and kinetics data for the modified CSS and the adsorption system was evaluated thermodynamically and from the energy point of view. Isothermal scrutinization indicated the mono-layer nature of adsorption, and the kinetics experimental outcomes best fitted with the pseudo-second-order, implying that the interaction of lead ions and hot acid-treated CSS was the rate-controlling phenomenon of process. Overall, results illustrated that the hot acid-treated biomass-based adsorbent can be considered as an alternative bio-adsorbent for removing lead from water media.

1. Introduction

Lead (Pb) may be discharged into water bodies through lead-containing industrial wastes from various industries such as electroplating and metal surface treatment processes (Hosseini-Bandegharai et al., 2016; Zahri et al., 2017; Azam et al., 2022; Kumar et al., 2022). Lead can lead to major health problems such as anaemia, lack of appetite, liver, kidney, and brain damage (Abbas et al., 2014). According to WHO guidelines, the maximum permissible Pb(II) ions concentration in drinking is 0.01 ppm (Kumar et al., 2022). Therefore, removal of Pb(II) ions from industrial wastewater has been a major concern for industries. Adsorption has been attracting attention for removal of heavy metals due to its simple operation, applicability over a wide operating conditions and possibility to develop adsorbents with high metal binding capacity (Bilal et al., 2021). Usually, a modification in functional groups or eliciting a morphological change can valorize and adsorbent for adsorption of heavy metal ions (Hosseini-Bandegharai et al., 2014; Anastopoulos et al., 2019; Alahabadi et al., 2020; Khaledi et al., 2022; Yadav et al., 2022). Modifying and utilizing biomass-based adsorbent for removal of heavy metals is an eco-friendly process and low-cost process (Dodbiba et al., 2015; Bhattacharjee et al., 2020; Jagaba et al., 2020; Bilal et al., 2021; Neme et al., 2022a).

Biomasses such as *pinus sylvestris* (Ucun et al., 2003), coffee grounds (Tokimoto et al., 2005), rice husk (Hossain et al., 2022) *aspergillus niger* (Amini et al., 2008) and ruit residual (Herald et al., 2018) have been investigated for removal of lead from water. Usually, the biomasses are treated with chemicals to improve their physiochemical properties and removal performances. Chemical modification of the biomasses helps to eliminate soluble organic substances and color forming components and permits exposure of more sorption sites embedded in the biomass (Ramrakhiani et al., 2016; Saxena et al., 2017; Abdel-Galil and El-kenany, 2018; Neme et al., 2022c). Various chemicals (acid, base, etc.) have been exploited for the purpose of treating lignocellulose materials to improvement their capacity in removing heavy metals from aqueous solutions (Deivasigamani et al., 2023; Musie et al., 2023). In the current work, castor (*Ricinus communis* L) seed shell was treated with phosphoric acid and exploited for Pb (II) ions removal from water. Phosphoric acid is less corrosive and creates less residue compared to other chemicals used for treatment of lignocellulose materials (Sajjadi et al., 2019; Neme et al., 2022b).

Castor plant is vastly grown in tropical, sub-tropical, and warm temperate areas and it is an indigenous to Eastern Africa, India and southeastern Mediterranean basin (Vasanthi et al., 2021; Neme et al., 2022c). Previously, Martins et al. (2013) used raw castor leave powder (without chemical treatment) for removal of heavy metal from water, including lead ions. Abdel-Galil and El-kenany (2018) used chemically treated castor stem for removal of lead ions and managed to attain 94% lead ions removal from aqueous solutions with initial lead concentration of 50 mg L^{-1} . This shows different parts of castor plant can be exploited as low-cost bio-adsorbent for removing lead ions from water. Hence, in

this work, castor seed shell was treated with phosphoric acid and applied for removing lead from water.

In the current work, we investigated adsorption of Pb(II) ions from water using raw castor seed shell (RCSS) and H_3PO_4 modified castor seed shell (MCSS). RCSS was treated with H_3PO_4 and it was characterized for morphological and physiochemical properties. Then, both the RCSS and MCSS were investigated for adsorption of Pb(II) ions from water at different adsorption parameters (pH, initial adsorbent concentration, time, adsorbent dose, and agitating speed). The adsorption parameters were optimized using central composite design based RSM to determine the optimum lead adsorption performance. Adsorption equilibrium data and kinetics data were fitted to different isothermal and kinetics models, respectively. The adsorption system was thermodynamically evaluated and the adsorption mechanism was brought under discussion.

2. Materials and methods

2.1. Chemicals and apparatus

Lead nitrate (99.9%), phosphoric acid (85%), potassium nitrate (99%), and 1,5-diphenylthiocarbazone (85%) were obtained from Sigma Aldrich. Hydrochloric acid, (37%), sodium hydroxide (98.5%) and acetone (99.9%) were supplied by Merck chemical. Castor seed was collected from Akaki area, Addis Ababa, Ethiopia.

2.2. Bio-adsorbent preparations

Castor seed shell was detached from the beans with knife and washed with tap water to remove dirt, soluble components and color. Then, it was dried overnight at 105 °C crushed and sieved to obtain powder with particles size in the range of 150–500 μm . Modification of castor seed shell powder was carried out at various H_3PO_4 concentrations (0.5, 1.0, 1.5, 2.0, 2.5, 3.0 M), solution-solid ratio (1.0, 3.0, 5.0, 7.0, 9.0 mL g^{-1}), activation time (40, 80, 120, 160 and 200 min) and activation temperature (50–120 °C). The castor seed shell powder was added to the acid solution in flask and mixed with magnetic stirrer at 180 rpm. Then, it was filtered and rinsed with distilled water and 1.0% of NaHCO_3 till the pH of the washing water becomes neutral. It was then dried in an oven at 105 °C overnight and stored in sealed plastic bags.

2.3. Characterizations

Proximate analyses of RCSS and H_3PO_4 modified CSS (MCSS) were performed according to ASTM standard (ASTM E870-82). FTIR (PerkinElmer V770, Japan) was recruited to analyze the alterations in functional groups of the raw and H_3PO_4 -treated castor seed shell. The morphological properties of RCSS and MCSS were examined using a SEM (INSPECTCT-F50, Germany) at 10 kV power, 750X magnification, and 20 μm . Crystallinities of the bio-adsorbents were investigated using

XRD (Shimadzu, XRD-7000) at 40 kV voltage and 44 mA current. The value radiation angle (2θ) was between 10 and 80° at $\lambda = 1.54 \text{ \AA}$.

2.4. Adsorption studies

Lead ions aqueous solution (1000 mg L^{-1} lead concentration) was built by adding dissolving lead (II) nitrate into distilled water. The working solutions were prepared at the desired concentrations by diluting the stock solution. The pH adjustments of the solutions were carried out using NaOH (0.1 M) and HCl (0.1 M). Batch adsorption experiments were carried out in 250 mL flasks by adding predetermined weight of bio-adsorbents to 100 mL solutions in the flasks. The absorptions were carried out for adsorbent dose (0.1, 0.4, 0.7, 1, and 1.3 g), pH (3, 4, 5, 6, and 7), time (30, 60, 90, 120, and 150 min), initial Pb(II) ions concentrations (50, 100, 150, 200, and 250 mg L^{-1}) and agitating speed (140–220 rpm). The bio-adsorbents were filtered out using filter paper after completion of each batch adsorption process. A filtrate sample (5 mL) was taken from each sample and mixed with 1 mL of 1,5-diphenylthiocarbazone (DPC) solution and acidified with 1.0 mL of H_2SO_4 solution. DPC solution was prepared by mixing 250 g DPC mixed with 50 mL of acetone. The Pb(II) ions concentration in the water was measured by UV-vis spectrophotometer (JASCO V-770, Japan). UV-vis spectrum was recorded at wavelength of 500 nm. Finally, Pb(II) ions removal percentage was calculated by Eq. (1).

$$\text{Removal (\%)} = \frac{C_i - C_f}{C_i} \times 100\% \quad (1)$$

where, C_i and C_f are the initial and final Pb (II) levels in water (mg L^{-1}). The adsorption capacity was determined using Eq. (2).

$$\text{Adsorption capacity} = \frac{(C_i - C_f) \times V}{M} \times 100\% \quad (2)$$

where, V is the volume of solutions (L) and M is the bio-adsorbent dose (g).

2.4.1. Response surface methodology

A model that shows the relationship between adsorption parameters and the response and interaction between the factors were developed using response surface methodology (RSM). Central composite design (CCD) based RSM was applied to generate models from experimental data. Design expert (Version 12) was employed to develop the model. The required number of experimental points for the CCD-based RSM can be calculated by $2^n + 2n + c$; where; n is the independent factors and c is the number of center points (Bayuo et al., 2019; Seid and Gonfa, 2022). Total of 30 experimental runs, including 6 center points, were performed to develop the model and the response surfaces. A 2nd order polynomial equation was fitted to establish the relation between the independent factors and response (Eq. (3)).

$$y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \quad (3)$$

where, y is the lead removal percentage (%), x_i is the independent factor (initial lead concentration, pH, contact time, or adsorbent dosage) and β_i is the coefficients. ANOVA was adopted to analyze the appropriateness of the model. Finally, three-dimensional response surface plots were created to visually see impacts of independent variables on the response. For the CCD-based RSM design, the minimum and maximum initial Pb (II) ion concentration were set to 100 and 200 (mg L^{-1}) and the minimum and maximum values for pH were 4.0 and 6.0. Similarly, the minimum and maximum contact time were fixed at 90 and 150 min while the values for adsorbent dose were 0.7 and 1.3 g/100 mL.

2.4.2. Adsorption isotherm

Langmuir, Freundlich isotherm and Temkin isotherm models were exploited to fit the experimental adsorption equilibrium data, along with

three three-parameter models (i.e., Sips, Redlich-Peterson, and Toth models).

The Langmuir model (non-linear form) is shown in Eq. (4).

$$q_e = \frac{Q_{\max}^0 + K_L C_e}{1 + K_L C_e} \quad (4)$$

where, $q_{\max}$ is maximum Pb(II) ions adsorption (mg g^{-1}), q_e is the lead adsorbed at equilibrium (mg g^{-1}) K_L is the Langmuir constant (L mg^{-1}), and C_e is the equilibrium Pb(II) ions concentration (mg L^{-1}). The $q_{\max}$ and K_L values are obtained from non-linear plot.

The Freundlich isotherm model can be given Eq. (5).

$$q_e = K_f C_e^{\frac{1}{n}} \quad (5)$$

where, k_f (mg g^{-1}) (L mg^{-1}) $^{1/n}$ is bonding intensity and n is the adsorption intensity. The k_f and n values are obtained from the non-linear plots.

The Temkin isotherm model can be represented by Eq. (6).

$$q_e = \frac{RT}{b} (\ln K_T C_e) \quad (6)$$

where b denotes the adsorption heat (J mol^{-1}), K_T represents the Temkin equilibrium binding constant (L g^{-1}), T is temperature (in Kelvin) and R gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

The Sips isotherm model can be given by Eq. (7).

$$q_e = \frac{q_{\max} (K_S \cdot C_e)^{\frac{1}{n}}}{1 + (K_S \cdot C_e)^{\frac{1}{n}}} \quad (7)$$

where n (dimensionless; Sips exponent), K_S ($\text{L}^n \text{ g}^{-n}$; Sips constant) and $q_{\max}$ (mg g^{-1} ; maximum Pb(II) ions adsorption) are obtained from non-linear plot.

Toth isotherm model can be given by Eq. (8).

$$q_e = \frac{q_{\max} K_T C_e}{[1 + (K_T C_e)^n]^{\frac{1}{n}}} \quad (8)$$

where, K_T (L mg^{-1}) is known as the Toth isotherm constant and n is the exponent of Toth isotherm.

The Redlich – Peterson isotherm model can be represented by Eq. (9).

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^n} \quad (9)$$

where n (dimensionless; Sips exponent), K_{R-P} (L g^{-1} ; Sips constant) and a_{RP} ($\text{L}^n \text{ mg}^{-n}$) are obtained from non-linear plot.

2.4.3. Adsorption kinetics study

Adsorption kinetics was studied by carrying out Pb(II) ions adsorption at various adsorption times (15, 40, 70, 90, and 110 min) keeping the other parapets at optimum points. A pseudo-first-order, pseudo-second order, and inter-particle diffusion kinetic models were employed to fit the kinetics data.

The pseudo-first-order kinetic model is given by Eq. (10).

$$q_t = q_e \cdot [1 - \exp(-K_1 \cdot t)] \quad (10)$$

where, q_e is the quantity of lead adsorbed at equilibrium condition (mg g^{-1}), q_t is the quantity of lead adsorbed at time t (mg g^{-1}) and k_1 is the equilibrium rate constant. By plotting the non-linear graphs, the values q_e and k_1 can be determined easily by the software.

The pseudo-second-order kinetic model can be represented by Eq. (11).

$$q_t = \frac{q_e^2 \cdot K_2 \cdot t}{[K_2 \cdot (q_e) \cdot t + 1]} \quad (11)$$

where, k_2 is the equilibrium rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). The k_2 and q_e were obtained by plotting non-linear graph.

Intraparticle diffusion model is presented by Eq. (12):

$$q_t = k_p t^{0.5} + c \quad (12)$$

where, k_p is the intraparticle diffusion constant ($\text{mg (g min}^{0.5})^{-1}$) and c (mg g^{-1}) is the boundary layer thickness which indicates the resistance to the mass transfer. The values of k_p and c can be obtained by drawing q_t versus t .

2.4.4. Error indices

To test the goodness-of-fit of each isotherm and kinetic model with the experimental outcomes, some statistical analyses (i.e., R^2 , ARE, Δq , and χ^2) were calculated from the related calculations (Mohammadzadeh et al., 2023; Naseri et al., 2023b; Peiravi-Rivash et al., 2023). Based upon highness of (R^2) on the lowness of other statistical indices, the best model was recognized for lead adsorption (Hosseini-Bandegharai et al., 2023).

2.4.5. Thermodynamic consideration

The feasibility and favorability of the adsorption process of lead ions was appraised by thermodynamic calculations. The correct dimensionless equilibrium constant (K_e) for such calculation was withdrawn from sips isotherm (Lima et al., 2019; Naseri et al., 2023a), using the following mathematical relations (Hu et al., 2023; Nouioua et al., 2023):

$$K_{S,M} = 1000 \times K_S \times AW_{Pb} \quad (13)$$

$$K_e = \text{numerical value of } K_{S,M} \quad (14)$$

where, AW is atomic weight of lead, K_S ($\text{L}^n \text{g}^{-n}$) is the Sips constant, $K_{S,M}$ ($\text{L}^n \text{mol}^{-n}$) is the molar Sips constant, and K_e (dimensionless) is the thermodynamic equilibrium constant (Shahryari et al., 2022; Naseri et al., 2023a).

3. Results and discussion

3.1. Characterization of raw and treated castor seed shell

The ash content of the raw and modified castor seed shell is lower than the value previously reported for castor seed hull and other biomass such as corn residue (Table 1). Moreover, the volatile component in raw and modified castor seed shell is lower than the values reported previously. The fixed carbon of the studied raw and modified castor seed shell is higher compared with values reported for most biomass. The result shows that treatment of the castor seed shell with H_3PO_4 enhanced the fixed carbon content and reduced the volatile components in the biomass.

The FTIR spectral analyses of RCSS and MCSS are depicted in Fig. 1a.

Table 1

Comparison of proximate values of RCSS and MCSS with other bio-adsorbent sources.

Adsorbent sources	MC (%)	Ash (%)	VM (%)	FC (%)	Reference
Raw castor seed hull	4.40	6.71	72.05	16.84	Neme et al. (2022c)
Raw corn residue	6.10	7.30	72.90	13.70	Neme et al. (2022c)
Treated corn residue	7.20	13.30	59.10	20.40	
RCSS	8.20	4.50	35.30	52.00	This study
MCSS	6.50	3.80	28.70	61.00	This study

MC: moisture content, VM: volatile matter, FC: fixed carbon.

Broad peaks were observed at a wavenumber of 3303.52 cm^{-1} and 3317.02 cm^{-1} for MCSS and RCSS, respectively. These peaks are due to the N-H group and OH stretching bands in biomass and water in the adsorbent (Al-Qodah et al., 2017; Castro et al., 2021). The wavenumber at 2886.96 cm^{-1} as well as 2816.28 cm^{-1} belong to the C-H stretching band in raw and modified biomass, respectively (Castro et al., 2021). In the RCSS, the peak at 1716.36 cm^{-1} was arisen because of compounds containing a C=O group in esters and carboxylic acids (Lee et al., 2018). Besides the hydroxyl group in MCSS, cyclic alkenes appeared in the wavenumber around 1604.51 cm^{-1} due to the shifting of functional group as well as thermal instability of C=O groups at a time of activation processes (Guo and Lua, 2002). Moreover, the peak at 528.41 cm^{-1} in the FTIR spectra of MCSS could be because of stretching vibrations of the P-O group, this shows that the phosphate acid was incorporated in CSS biomass (Al-Qodah et al., 2017). In general, some shifted their band due to thermal instabilities during the modification process, which was carried out at high temperatures relative to the surroundings.

The SEM images for RCSS and MCSS bio-adsorbents are provided in Fig. 1b and c, respectively. The SEM image shows the surface morphology of RCSS, which was relatively smooth surface due to the presence of strong un-broken cellulose, hemicelluloses, and lignin materials (Soedarmanto et al., 2020). The SEM image of modified castor seed shell was also included in the supplementary material (Figure S2). The SEM image shows more openings and rough surfaces on the modified castor seed shell compared to the raw castor seed shell. This is due to the breaking down of lignin, cellulose and hemicellulose linkages and removal of volatile components from the biomass (Soedarmanto et al., 2020; Neme et al., 2022c).

The patterns XRD for RCSS and MCSS are indicated in Fig. 1d and e, respectively. The XRD pattern of RCSS which have a crystalline peak under the specified range of 2θ of 34.84° , and 58.02° whereas a broad peak formed at of 2θ of 13.72 – 17.48° and 19.75 – 24.16° . This shows the existence of the amorphous structure like other lignocellulosic biomasses (Liao et al., 2011). The XRD results of the MCSS shown indicates that there are more sharp crystalline peaks formed around 2θ of 31.72° , 56.5° , and 66.7° . These crystalline peaks were favored more in the MCSS as compared to the amorphous nature of RCSS due to the decomposition of lignocellulose material (lignin and hemicellulose) during the time of modification process (Akindolie and Choi, 2023). The increased crystallinity of castor seed shells was due to the removal of volatile components during chemical treatment processes.

3.2. Adsorption studies

3.2.1. Effects of impregnation parameters

The impact of impregnation parameters on the performance of the bio-adsorbent is depicted in Fig. 2. The impact of acid concentration on the Pb (II) removal performance of MCSS is displayed in Fig. 2a. The effect of H_3PO_4 impregnation concentration was investigated for acid concentrations of (0.5, 1.0, 1.5, 2.0, 2.5, and 3 M) keeping the impregnation ratio, temperature and time at 5 mL g^{-1} , 95°C , and 160 min, respectively. As can be seen, the Pb(II) adsorption capacity increases from 7.90 to 11.46 mg L^{-1} as H_3PO_4 concentration increases from 0.5 to 2 M. However, a further increase in H_3PO_4 concentration reduces the adsorption capacity.

The impact of the impregnation ratio on the lead adsorption capacity is depicted in Fig. 2b. The effect of impregnation ratio over 1.0–9.0 mL g^{-1} keeping acid concentration, temperature, and impregnation time at 2 M, 95°C , and 160 min, respectively. It was observed that the adsorption capacity raised sharply from 7.02 to 11.06 mg L^{-1} as the impregnation ratio increased from 1.0 to 5.0 mL g^{-1} . Then, the value gradually changed from 11.06 to 11.12 mg L^{-1} when the ratio increased to 7 mL g^{-1} . However, excessive acid impregnation may result in accumulation of acid on the surface of the adsorbent and filling of the pore so which can reduce adsorption capacity of the bio-adsorbent.

Fig. 2c shows the impact of activation time over a time interval from

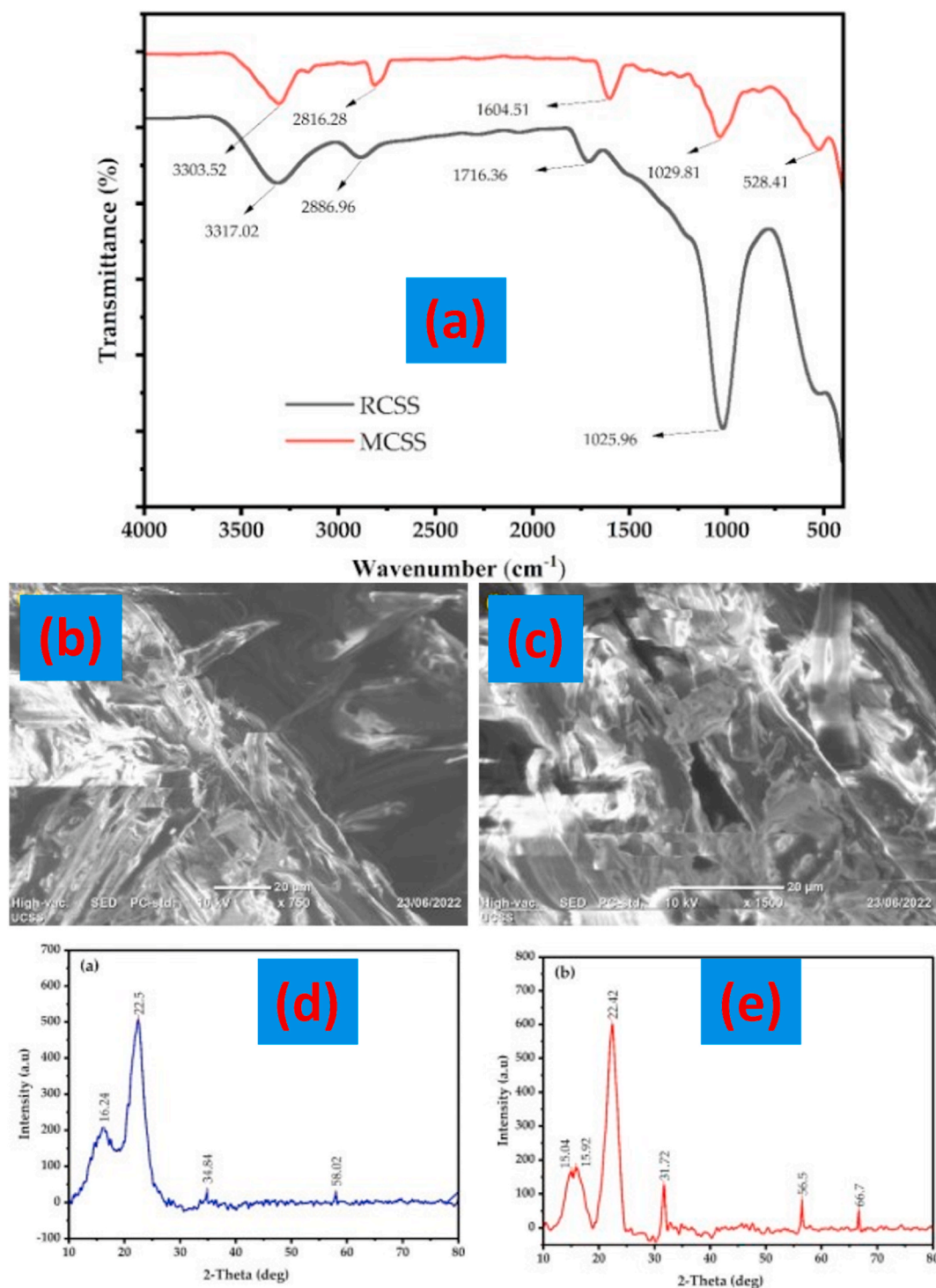


Fig. 1. FTIR spectra of RCSS and MCSS bio-adsorbent (a); SEM surface morphology images of RCSS (b) and MCSS (c); and XRD patterns of RCSS (d) and MCSS (e).

40 to 200 min while keeping the acid concentration, impregnation ratio, temperature and time at 2 M, 5 mL g^{-1} , 95 °C and 160 min, respectively. The Pb(II) ions removal percentage increases from 6.28 to 11.05 mg L^{-1} over a period of 160 min. As the acid activation time increases up to 160 min the volatile matter from the biomass increases. However, excess treatment time may result in damage to the biomass structure and reduction of porosity and pore volume of the bio-adsorbent.

The impact of temperature on the performance of the bio-adsorbent was studied over the range of 50–120 °C. Fig. 2d shows that 11.18 mg L^{-1} of adsorption capacity of bio-adsorbent was achieved at 95 °C,

which was the highest value. The adsorption capacity augmented from 6.72 to 11.18 mg L^{-1} as the activation temperature reached 95 °C. Further, increasing temperature causes its value to drop to 9.22 mg L^{-1} because the increasing activation temperature beyond the optimum point had a detrimental impact on the development of internal pores due to excessive burn-off, and certain microspores became meso- or even macrospores.

3.2.2. Effects of adsorption parameters

Fig. 3 shows the effects of major adsorption parameters on lead

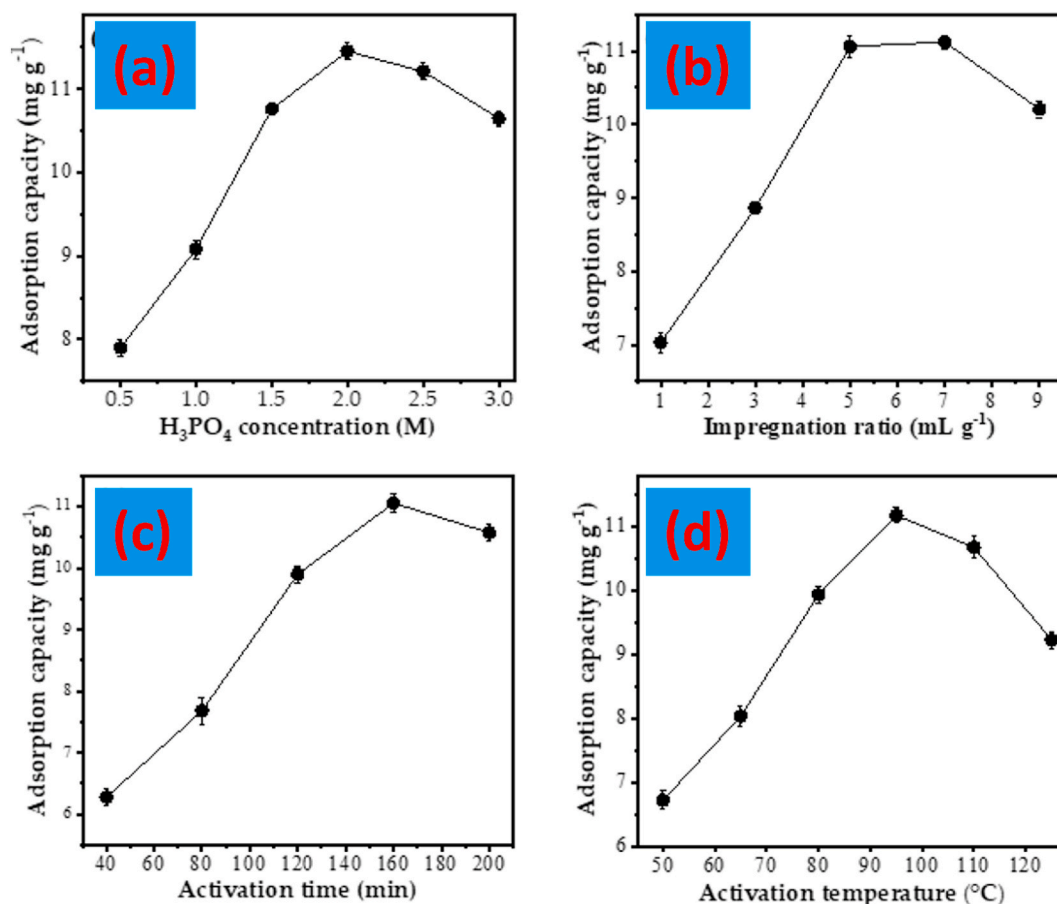


Fig. 2. Effects of acid treatment parameter parameters on Pb(II) adsorption capacity: (a) H₃PO₄ concentration, (b) impregnation ratio, (c) time and (d) temperature.

percent removal at room temperature. The effect of initial lead level was appraised by altering Pb(II) ions level from 50 to 250 mg L⁻¹ at a constant adsorbent dose (1.0 g), pH (5.4) and adsorption time (150 min). Fig. 3a shows that a maximum of 96.97% removal was achieved at an initial level of 50 mg L⁻¹ whereas the value reduced to 66.51% as the initial level increased to 250 mg L⁻¹. Such result is because there may be limited adsorption sites to accommodate high lead ions concentrations. The impact of pH on Pb(II) removal was investigated over a pH range of 3.0–7.0. Fig. 3b demonstrates the influence of pH on the percent removal of Pb(II) ions. As pH increased from 3.0 to 5.0, the value of percent lead removal increases from 77.4 to 97.32% and then gradually decreases. At pH below pH_{pzc} (4.9), the adsorbent surface is surrounded by more H⁺ ions which hinder Pb(II) ions interaction with the adsorbent binding sites (Jalu et al., 2021). Therefore, the removal efficiency will be low. At higher pH, OH⁻ ions compete with lead ions and reduce their adsorption on the adsorbent's surface (Ketsela et al., 2020). Hence, lower and higher pH reduce the Pb(II) ions adsorption capacity MCSS. On the other hand, at higher pH lead ions starts to precipitate in the form of different hydroxide products and making true adsorption studies impossible (Erentürk and Malkoç, 2007).

Fig. 3c shows the effect of time with time over a range of 30–150 min on adsorption of Pb(II) ions on bio-adsorbents. The rate of lead adsorption was rapid in the first 60 min. The Pb (II) ion removal increases from 74.25 to 98.14% as the contact time increases from 30 to 90 min this is related to availability of a higher number of active sites at initial adsorption stages (Foroutan et al., 2020). After 90 min, there was no imperative augmentation in removal percentage. Maximal removal efficacy of 98.14% was acquired at a contact duration of 120 min. After the optimum time, there is no increment in the lead percent removal since there are no additional free active sites and adsorption takes place

at equilibrium condition (Foroutan et al., 2020).

The impact of MCSS dosage on adsorption of Pb(II) ions was investigated over bio-adsorbent dosage to solution ratio of (0.1–1.3 g)/100 mL as shown in Fig. 3d. The percent lead ions removal increased from 71.72 to 95.17% as the quantity of adsorbent increased to 0.70 g. The value then gradually increased maximum of 97.0% at adsorbent dose of 1.0 g. The increase in adsorption percentage with an augmentation in adsorbent dose was because of availability of more adsorbent sites as the MCSS dose increased (Saha et al., 2010). Further increase of the dosage could not affect the removal percentage as the majority of the lead ion adsorbed on an excess number of adsorbent sites, and almost a negligible amount of it was left in the solution (Munir et al., 2020). As a result, adding more than 1.0 g of the adsorbent to the aqueous solution could not affect the removal efficiency significantly. Mixing is an imperative factor in the batch adsorption process as it influences agitation of solution and mass transfer process (Saha et al., 2010). The impact of mixing on the Pb(II) ions percent removal was investigated at agitation speeds ranging from 140 to 220 rpm. Fig. 3e indicates the effect of mixing speed on the lead percent removal. Its removal percentage increases from 93.79 to 96.98% when the mixing speed increases to 220 rpm and 96.98% of the maximum removal was achieved at an agitator speed of 200 rpm. Further increasing the mixing speed has a negative impact on the response. Hence, at high agitating speed, the adsorbed metal ion experiences a strong centrifugal force which causes the desorption of the lead ion from the adsorbent surface (Saha et al., 2010).

3.2.3. Experimental design and statistical analysis

The impacts of four adsorption parameters (initial level of lead, pH, time, and adsorbent dose) were investigated, recruiting central composite design (CCD) based response surface methodology (RSM). The

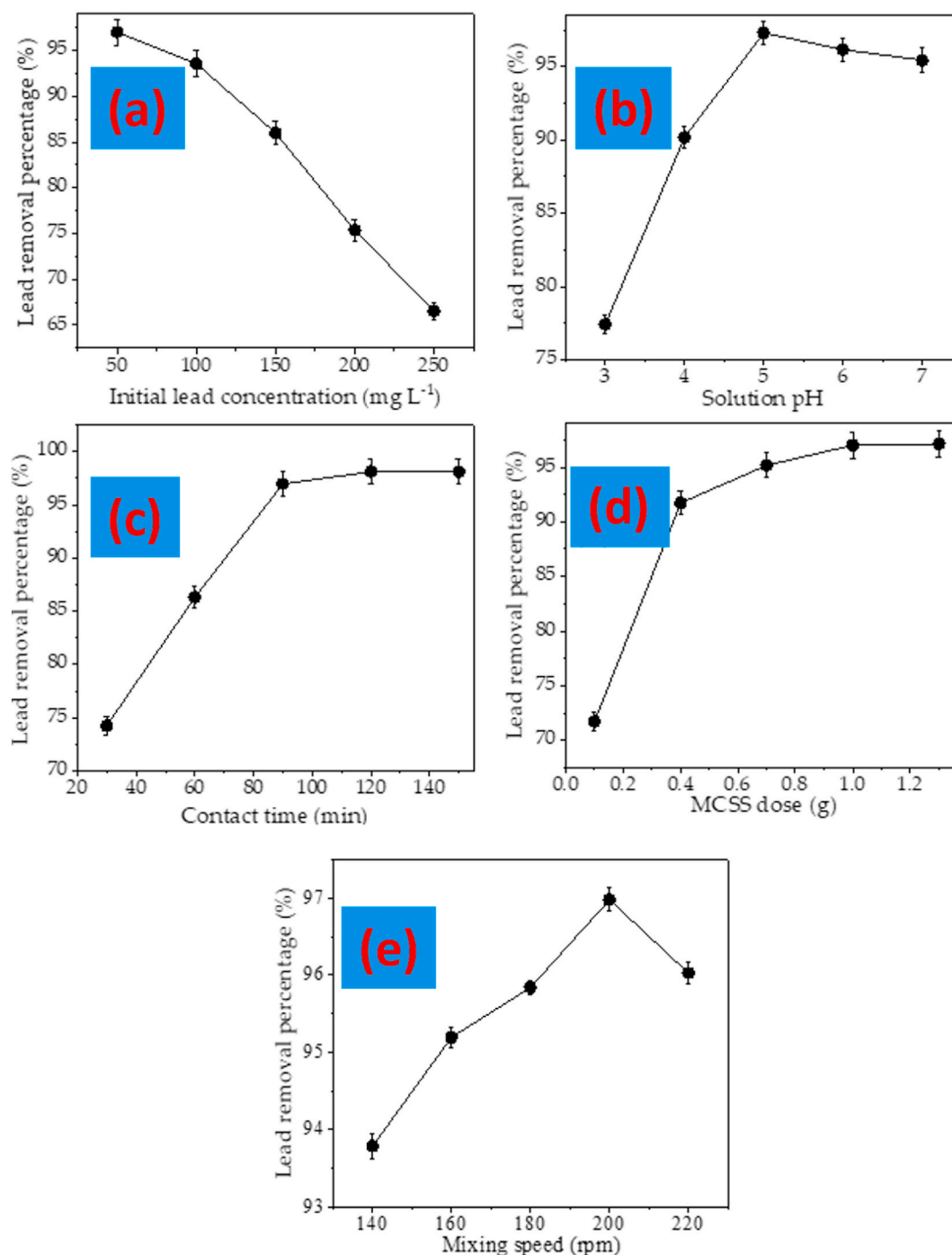


Fig. 3. Impact of adsorption parameters on lead removal percentage. (a) Initial lead concentration, (b) pH, (c) time, (d) bio-adsorbent dose and (e) mixing speed.

mixing speed was kept constant at 200 rpm. The values of the experimental and predicted Pb(II) ions removal percentages are depicted in Table 2. The experimental lead removal percentage varies from 65.51 to 97.45%. The relationship between the four independent factors and the Pb(II) ions removal percentage (response) was using second-order polynomial equation. The symbols A, B, C and D stand for Pb (II) ions initial level, solution pH, contact duration, and adsorbent dosage. The correlation coefficient (R^2) of the model fitted is 0.9955 which shows reasonable model fitting. The model fit and summary statistics, analysis of variance (ANOVA) analyses and experimental design matrix generated by CCD for pb (ii) ions removal of the established model were presented in supplementary material (Table S1, S2 and S3).

$$\begin{aligned}
 R(\%) = & 94.8304 - 5.55246A + 4.97214B + 3.06644C + 2.34195D \\
 & + 1.63793AB + 0.252743AC + 1.27155AD - 0.23315BC \\
 & + 1.27155BD - 1.58307CD - 2.28287A^2 - 3.7115B^2 - 2.41317C^2 \\
 & - 1.51976D^2
 \end{aligned}
 \quad (15)$$

The 3D plot surfaces for the four factors against Pb(II) ions removal percentage, taking two process variables at a time, are depicted in Fig. 4. Fig. 4a displays the impact of pH and initial Pb(II) ions concentration. Minimum removal percentages are observed at lower pH and higher initial concentrations. The removal percentage increases with increasing solution pH to some level and with decreasing the initial concentration

Table 2

Experimental design matrix generated by CCD for pb (II) ion removal.

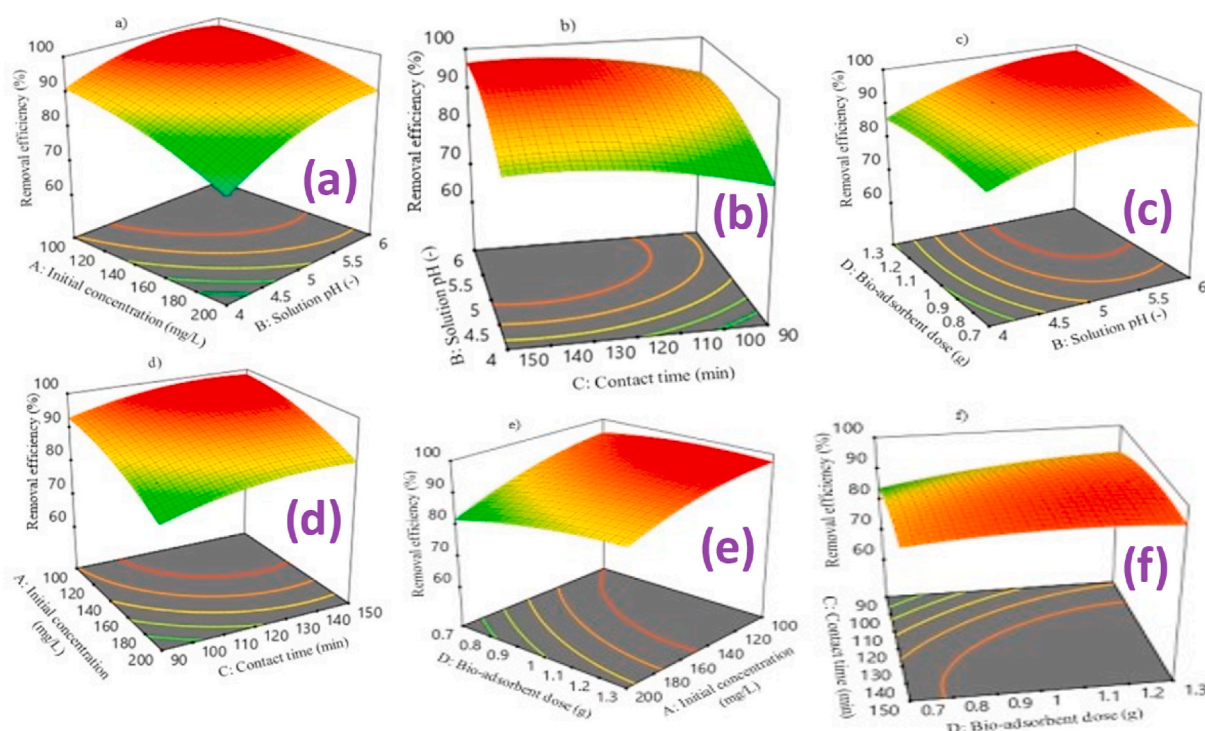
Run	Factors				Pb(II) ions removal percentage (%)	
	A	B	C	D	Experimental	Predicted
1	100	4	150	0.7	92.11	91.95
2	100	6	150	0.7	95.53	95.61
3	150	7	120	1.0	90.20	89.93
4	100	6	90	1.3	95.12	95.13
5	150	5	180	1.0	91.61	91.31
6	100	6	150	1.3	96.56	97.13
7	200	4	150	0.7	75.54	75.53
8	200	4	150	1.3	76.98	77.05
9	150	5	120	1.0	95.03	94.83
10	50	5	120	1.0	97.45	96.80
11	150	5	120	1.0	94.80	94.83
12	150	3	120	1.0	70.10	70.04
13	100	6	90	0.7	87.03	87.28
14	150	5	120	1.0	95.18	94.83
15	100	4	90	0.7	82.42	82.69
16	100	4	90	1.3	85.31	85.46
17	200	4	90	0.7	65.51	65.26
18	150	5	60	1.0	79.09	79.04
19	200	4	90	1.3	73.19	73.11
20	200	6	90	0.7	76.84	76.41
21	250	5	120	1.0	74.29	74.59
22	150	5	120	1.0	95.03	94.83
23	200	6	150	0.7	85.57	85.74
24	150	5	120	0.4	83.87	84.07
25	200	6	90	1.3	88.86	89.34
26	150	5	120	1.0	94.66	94.83
27	200	6	150	1.3	92.61	92.35
28	100	4	150	1.3	87.94	88.38
29	150	5	120	1.0	94.28	94.83
30	150	5	120	1.6	93.97	93.44

The p-value which is less than 0.05 shows that the terms in the model are significant. All the terms (A, B, C, D, AB, AC, AD, BC, BD, CD, A², B², C², and D²) are significant terms because their p-values are less than 0.05. The empirical relationship between Pb(II) ions removal percentage (R) as a response and the input variables is given by Eq. (15).

of lead ions. Finally, the highest percentage removal was achieved at a relatively higher pH and low initial concentration. Fig. 4b indicates impacts of contact duration and pH on the lead percent removal. Lead percent removal increases with increase in contact duration to some level is reached. Then, it became constant with further increases in contact duration because the net rate of the adsorption-desorption process becomes zero. The minimum removal efficiency was observed at a lower solution pH and lower contact time. On the other hand, the percent removal increases with increasing pH and contact time up to some levels. Generally, the maximum removal percentage was achieved at a relatively higher pH and adsorption time.

Fig. 4c illustrates a 3D plot that displays the impact of pH and bio-adsorbent dose on the removal percentage of lead from water. The removal percentage increases with the increasing in pH and adsorbent dosage until its pH reaches 5.0 and dosage reaches 1.0 g. Then, the percentage starts to reduce gradually as the pH and adsorbent dosage further increase. The 3D surface plot of the combined impact of initial concentration and contact duration is demonstrated in Fig. 4d. As the contact time increases from 90 to 120 min, its response increases. However, the lead percent removal reduces as the initial concentration increases. The interaction impact of initial lead ions level and MCSS dose was demonstrated in Fig. 4e. The response decreases as the initial Pb (II) ions concentration increases while it increases with increasing adsorbent dosage. The interaction impact of dose and contact time was represented in Fig. 4f. It shows the response increases as both adsorbent dose and contact time increase.

The response surface methodology model provided an optimum Pb (II) ions removal of 98.09% at initial lead concentration (146.55 mg L⁻¹), pH (5.68), bio-adsorbent dose (1.14 g) and time (122.78 min). To validate the optimization results, which were obtained from the CCD-based RSM model, triplicate tests were conducted at optimal conditions. The experimental lead removal percentage at initial lead concentration (146.55 mg L⁻¹), pH (5.68), bio-adsorbent dose (1.14 g) and time (122.78 min) is 97.62%. This shows the actual experimental values in good agreement with the anticipated value. This implies the developed model can reasonably predict the lead removal percentage from water using the MCSS bio-adsorbent. Finally, the performance of raw

**Fig. 4.** 3D surface plots of interaction effects of adsorption parameters.

castor seed shell (RCSS) and H_3PO_4 modified castor seed shell (MCSS) were compared to each other at similar adsorption conditions. The adsorption was carried out at Pb(II) ions initial concentration of 146 mg L^{-1} , pH of 5.7, contact time of 123 min and bio-adsorbent dosage of 1.1 g/100 mL lead solution. The result shows a removal percentage of 72.26% for the raw castor seed shell while the value for the treated shell is 97.62%. This shows modification of the castor seed shell enhances its lead removal capacity.

3.2.4. Adsorption isotherm study

Adsorption behavior lead on the modified bio-adsorbent was studied using isotherm models. For this purpose, the lead adsorption isotherm experiments were carried out by varying its levels from 30 to 250 mg L^{-1} while keeping other parameters constant at optimum points. Langmuir, Freundlich and Temkin isotherm models were then fitted to equilibrium adsorption data and indicated in Fig. 5a, to see whether two-parameter models are suitable for describing the adsorption process (Narayanan et al., 2022; Abidin et al., 2023). Also, for better scrutinization of adsorption process, three three-parameter models were fitted with the data (Fig. 5a). Amongst two-parameter models, the Langmuir plot indicates the highest R^2 value of 0.9933 with low values of ARE (0.38%), Δq (6.17%), and χ^2 (0.18) (Table 3). Freundlich model, on the other hand, shows the lowest R^2 of 0.8914 with high values of ARE (11.59%), Δq (34.05%), and χ^2 (2.64). Such findings reveals that the adsorption process does not obey from a multi-layer mechanism, and the equilibrium data should be appraised by three-parameter models for better interpretations. Having a glimpse on the results reported in Table 3 shows that all three-parameter equations have high R^2 values which are almost commensurate with that of Langmuir model. Additionally, the assessed statistical indices are also low and are close to those of Langmuir model. Although the R^2 value (0.9939) and values of ARE (0.33%), Δq (5.72%), and χ^2 (0.16) obtained for Sips model indicate that this model is a little bit more successful in fitting the experimental data, the n value of Sips and even other three-parameter models are near to unity which cause collapsing this model to the Langmuir model (Shahryari et al., 2022; Sunkar et al., 2023).

Indeed, the data reported in Table 3 vouchsafe that adsorption of lead on MCSS best fits to Langmuir model with a maximum adsorption capacity of 21.18 mg g^{-1} , indicating a mono-layer adsorption which usually is characteristic property of heavy metal adsorption on biomass-based adsorbents (Alahabadi et al., 2020; Rahmani-Sani et al., 2020; Deivasigamani et al., 2023). From the Freundlich isotherm model, the value of the Freundlich constant (n) indicates the adsorption intensity of the adsorbent-adsorbate system. In Table 3, the value of $1/n$ for lead ion adsorption was found to be 0.35, which was under the range of 0–1.0, implying strong interaction between the lead ion and modified bio-adsorbent (Jia et al., 2019).

3.2.5. Adsorption kinetic study

The kinetics studies performed by varying the contact time of 15, 40, 70, 90, and 110 min on Pb(II) ions removal using the modified bio-adsorbent, using a 100 mL solution with Pb level of 100 mg L^{-1} and a adsorbent dose of 0.6 g. The outcomes of fitness of experimental finding with pseudo-first order (PFO) and pseudo-second order (PSO) models are illustrated in Fig. 5b. The results were used to determine which model best fits data, by comparing the correlation coefficients and statistical indexes. The pseudo-first-order kinetics model is shown in Fig. 5b. The values of these kinetics model constants were calculated from the non-linear curves their mathematical relations (Table 4). PSO equation demonstrated a higher R^2 value (0.9996) with lower values of ARE (0.07%), Δq (2.63%), and χ^2 (0.04), compared to PFO model whose R^2 , ARE, Δq , and χ^2 were respectively 0.9945, 0.19%, 4.40%, and 0.08. The pseudo-second-order kinetics model fits to kinetic data with better statistical data and closeness of q_e value with the experimental value (19.08 mg g^{-1}) means that Pb(II) ion-adsorption site interaction is the

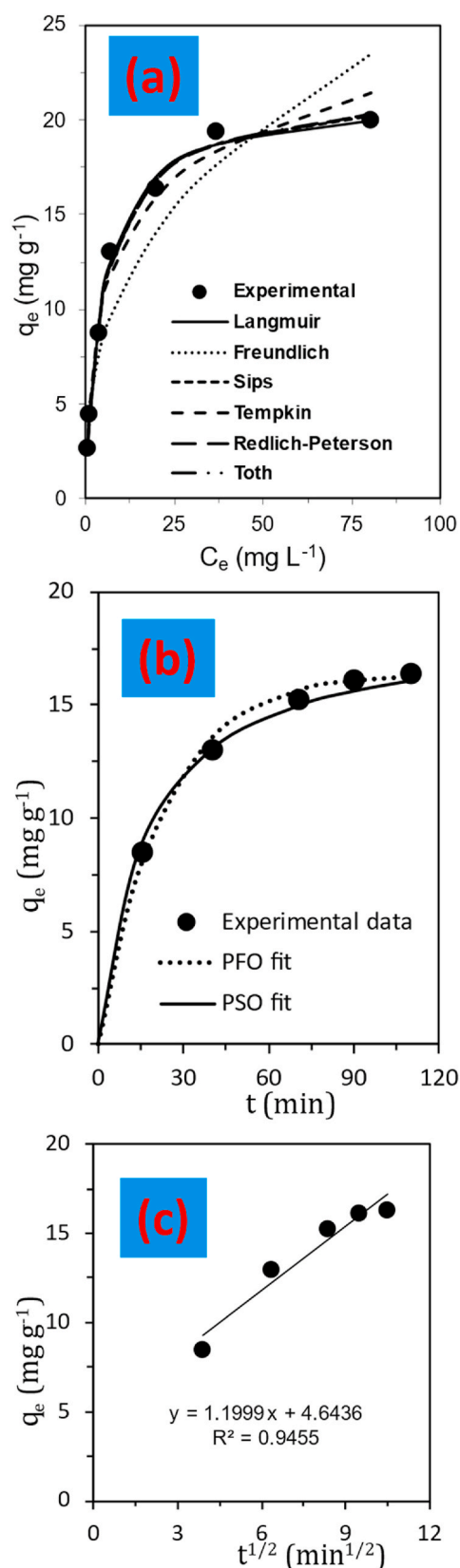


Fig. 5. Visual evaluation of fitness of equilibrium outcomes with different isotherms (a), visual evaluation of fitness of kinetic's outcomes with PFO and PSO equations (b), and visual evaluation of fitness of intra-particle diffusion with kinetic's outcomes (c).

Table 3
Isotherm model constants for adsorption of lead on MCSS.

Isotherm model	Parameter or index	Values
Langmuir isotherm	$q_{\max}$ (mg g ⁻¹)	21.18
	b (L mg ⁻¹)	0.21
	R^2	0.9933
	ARE	0.38
	% Δq	6.17
Freundlich isotherm	χ^2	0.18
	k_f (mg g ⁻¹) (L mg ⁻¹) ^{1/n}	5.24
	$1/n$	0.35
	R^2	0.8914
	ARE	11.59
Temkin isotherm	% Δq	34.05
	χ^2	2.64
	b (J mol ⁻¹)	3.99
	K_T (L g ⁻¹)	2.75
	R^2	0.9806
Toth isotherm	ARE	0.47
	% Δq	6.89
	χ^2	0.36
	$q_{\max}$ (mg g ⁻¹)	22.10
	K_T (L mg ⁻¹)	0.22
Redlich-Peterson isotherm	n	0.89
	R^2	0.9937
	ARE	0.32
	% Δq	5.68
	χ^2	0.16
Redlich-Peterson isotherm	K_{R-P} (L g ⁻¹)	4.60
	n	0.97
	a_{RP} (L ⁿ mg ⁻ⁿ)	0.24
	R^2	0.9934
	ARE	0.33
Sips isotherm	% Δq	5.78
	χ^2	0.17
	$q_{\max}$ (mg g ⁻¹)	21.87
	K_S (L ⁿ mg ⁻ⁿ)	0.18
	n	0.94
Sips isotherm	R^2	0.9939
	ARE	0.33
	% Δq	5.72
	χ^2	0.16

Table 4
Kinetic model parameter in indexes on non-linear fit for adsorption of lead on MCSS.

Kinetics model	Parameter and indexes	Values
Pseudo-first order	q_{eq} (mg g ⁻¹)	16.36
	k_f (min ⁻¹)	0.044
	R^2	0.9945
	ARE	0.19
	% Δq	4.40
Pseudo-second order	χ^2	0.08
	q_{eq}	18.40
	k_s (g mg ⁻¹ min ⁻¹)	0.003
	R^2	0.9996
	ARE	0.07
Intra-particle diffusion	% Δq	2.63
	χ^2	0.04
	K_{di} (mg g ⁻¹ min ^{-1/2})	1.20
	C (mg g ⁻¹)	4.64
	R^2	0.9455

rate-controlling stage among the possible stage which can control the rate of the whole process (de Oliveira et al., 2023; Peiravi-Rivash et al., 2023).

In addition to the above scrutinization, the particle diffusion model was analyzed by plotting q_t versus $t^{1/2}$ (Fig. 5c). The intra-particle diffusion model does not have a good fit with kinetic data in entire range of evaluated time, since the R^2 value is 0.9455 which is low. On the other hand, the value of C is quite large which again demonstrate the lack of fitness of experimental findings with the model in the entire

range of studied time. One cannot claim that the particle diffusion has no effect on the kinetic aspects, since many adsorptions system obeying the PSO model are affected by intra-particle diffusion (Hosseini-Bandegharai et al., 2010, 2014; Khamirchi et al., 2018). In fact, the plot of q_e against $t^{1/2}$ can be divided to several parts, in which the R^2 values of linear plots will be quite large for each part, implying the impact of porous structure on the kinetic properties of the process.

3.2.6. Thermodynamic evaluation and adsorption energy

The spontaneity and favorability of the adsorption process can be appraised by thermodynamic evaluation. Hence, using Eqs. (13) and (14) and Sips isotherm constant, the dimensionless constant (K_e ; 37.29 $\times 10^3$) was computed at ambient temperature (298 K) and used for thermodynamic assessment of the adsorption process. The following equation was exploited for this purpose (Lima et al., 2019):

$$\Delta G^\circ = -RT \ln K_e \quad (16)$$

where, K_e is the correct thermodynamic equilibrium constant (dimensionless) (Naseri et al., 2023b; Nouioua et al., 2023), ΔG° (kJ mol⁻¹) is the change in free energy of Gibbs during the adsorption, T (K) is the temperature of adsorption system, R (8.314 J mol⁻¹ K⁻¹) is the universal gas constant. The ΔG° obtained for the adsorption system was -26.09 kJ mol⁻¹. The negativity of this parameter shows that the process is both spontaneous and feasible (Hu et al., 2023).

Using the following relation (van't Hoff equation), values of ΔH° (kJ mol⁻¹) and ΔS° (kJ mol⁻¹ K⁻¹) can be calculated from the slope and intercept of the plot of $\ln K_e$ vs $1/T$ (Djekoune et al., 2024; John et al., 2024):

$$\ln K_e = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (17)$$

Therefore, by repeating the isothermal data at two other temperatures (308 and 318 K), the K_e values were calculated at these temperatures, and the values were utilized in the van't Hoff equation for thermodynamic calculations (Fig. 6). At various temperatures at higher temperatures (308 and 318 K), the calculated ΔG° values were -27.79, and -29.43 kJ mol⁻¹, respectively, revealing the more favorability of the process at the higher temperature and its endothermic nature. The obtained values for ΔH° and ΔS° were 26.89 kJ mol⁻¹ and 167.73 kJ mol⁻¹ K⁻¹, respectively. Based the value of ΔH° (26.89 kJ mol⁻¹), it may be concluded that some physisorption forces, like cation- π interactions, along with some physiochemical forces, like ion-exchange and chelating

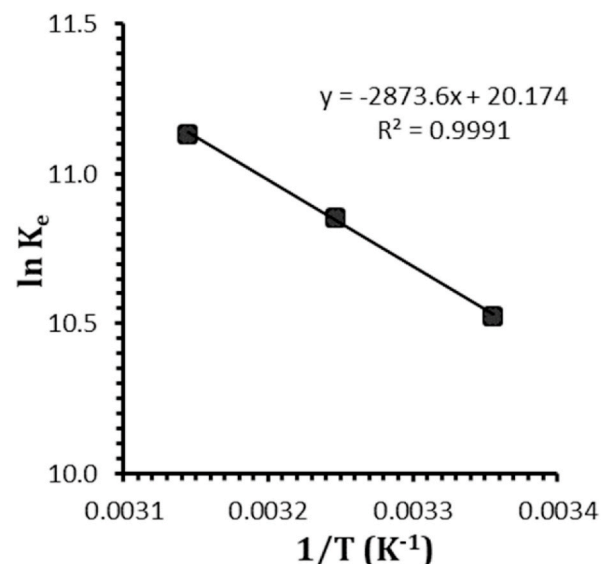


Fig. 6. The plot of $\ln K_e$ vs. $1/T$.

ion-exchange, are responsible in Pb(II) ion adsorption process (Shah-yari et al., 2022). Also, the positive value of ΔS° indicates an increase in randomness during the sorption process—possibly as a result of releasing the solvated water molecules at the liquid-solid interface (Peiravi-Rivash et al., 2023).

The adsorption energy can be estimated from D-R (Dubinin-Radushkevich) equation. This isotherm can be represented as the following equation (Peiravi-Rivash et al., 2023):

$$q_e = q_{D-R} e^{-K_{DR} \varepsilon^2} \quad (18)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (19)$$

where K_{D-R} ($\text{mol}^2 \text{kJ}^{-2}$) is Dubinin–Radushkevich constant which is related to the energy of adsorption, ε (kJ mol^{-1}) is the Polanyi potential (adsorption potential), T (K) the adsorption system's temperature, and R ($\text{J mol}^{-1} \text{K}^{-1}$) shows the universal constant of gases. At any temperature, E_{D-R} (kJ mol^{-1} ; the mean energy of adsorption) can be estimated by the following relation:

$$E_{D-R} = \frac{1}{\sqrt{2K_{D-R}}} \quad (20)$$

The measured E_{D-R} was 0.33 kJ mol^{-1} , suggesting the physisorption being the dominant mechanism of adsorption of Pb^{+2} on the adsorbent, since the value is $< 8 \text{ kJ mol}^{-1}$. Considering the nature of the H_3PO_4 -treated castor seed shell and the above results, one can conceive that the adsorption of lead ions in this system is dominantly proceeded via cation- π interactions, ion-exchange, and chelating ion-exchanges, as were supported by the value of ΔH° value mentioned earlier.

4. Conclusions

In this study, preparation and characterization of bio-adsorbent from was carried out and its adsorption performance for removal of lead from aqueous solution was investigated. Castor seed shell waste was treated by hot H_3PO_4 and the performance of the adsorbent was appraised, scrutinizing adsorption properties. The FTIR, SEM, and XRD analyses demonstrate changes in the morphology and functional groups of the biomass due to the acid modification. H_3PO_4 concentration, impregnation ratio, activation time and activation temperature show positive effects on the adsorption capacity of the modified bio-adsorbent until values reach 2 M, 5 mL g^{-1} , 160 min and 95°C . An optimum lead removal of 72.26% for raw castor seed shell and 97.62% for H_3PO_4 treated castor seed shell were attained at initial lead concentration 50 mg L^{-1} , at optimal pH (5.7), time (123 min), and adsorbent dose (1.1 g). Moreover, the kinetic aspects, along equilibrium and thermodynamic scrutinization showed that treatment of castor seed shell with hot H_3PO_4 can improve the adsorption characteristics and adsorption performance of bio-adsorbent.

Availability of data and materials

All data will be made available on request.

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CRediT authorship contribution statement

Mulusew Alehegn: Data curation, Writing – original draft. **Girma Gonfa:** Conceptualization, Methodology, Writing – review & editing. **P. A. Vivekanand:** Writing – review & editing. **Basant Lal:** Writing – review & editing. **Omirserik Baigenzhenov:** Software, Writing – review

& editing. **Ahmad Hosseini-Bandegharai:** Writing – review & editing. **Dmitry Olegovich Bokov:** Writing – review & editing. **Galiya Baisalova:** Data curation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2024.142655>.

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